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(56) Documents Cited

**GB 1567767 A GB 1459284 A US 5445741 A**  
**WPI Abstract Accession No. 94-221535 & JP 6157007**

(58) Field of Search

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(54) Abstract Title

**Process for the purification of brines**

(57) Process for the purification from organic compounds of an aqueous solution, according to which:

- (a) the pH of the solution is brought to at least 13;
  - (b) the solution is heated at at least 100°C for at least 1 hour;
  - (c) at least one chlorine-comprising oxidizing agent is gradually added to the solution.
- The solution to be purified may contain a sulphonium ion.

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Process for the purification of brines

The present invention relates to a process for the purification from organic compounds of aqueous solutions and in particular of brines.

The aqueous solutions collected as effluents from organic synthesis processes are often laden with troublesome organic compounds, the removal of which is desirable in many cases and very particularly in the case of brines, the exploitation of which by electrolysis in plants equipped with ion-exchange membranes is envisaged, for example for the purpose of producing aqueous sodium hydroxide solutions. This is because several organic compounds seriously affect the performances of the said membranes, in particular the trimethylsulphonium cation ( $(\text{CH}_3)_3\text{S}^+$ ).

Processes for the removal of organic compounds, for example chlorination processes, are certainly known but these known processes do not make it possible satisfactorily to reduce the content of organic compounds (as measured, for example, by the total organic carbon content, commonly known as "TOC") in the aqueous solutions. In addition, these known processes are ineffective with regard to certain specific organic compounds, for example trimethylsulphonium salts.

Provision has already been made to subject waste water comprising undesired organic substances to an oxidative chemical treatment with heating, the said substances being thus oxidized to carbon dioxide and water. Such a process, disclosed, for example, in the document DE 26 40 603, is generally known under the name of wet oxidation.

The wet oxidation process is comparable with a liquid phase combustion. To achieve satisfactory decomposition of the organic compounds and adequate conversion rates, a predetermined concentration of oxygen as well as high temperatures and high pressures are necessary. This treatment process is therefore very expensive because of its high energy consumption and the expensive equipment used. The temperatures and the

pressures employed can certainly be reduced by the addition of catalysts based on heavy metals but this leads to an additional purification stage in order to remove these catalysts.

5       The present invention is consequently targeted at providing a process for the purification from organic compounds of aqueous solutions which is simple and efficient, both in terms of the variety of the organic compounds removed and in terms of the final  
10 contents of organic compounds in the solutions.

To this end, the present invention relates to a process for the purification from organic compounds of an aqueous solution, according to which:

- (a) the pH of the solution is brought to at least 13;
- 15 (b) the solution is heated at at least 100°C for at least 1 hour;
- (c) at least one chlorine-comprising oxidizing agent is gradually added to the solution.

This process can take place continuously or  
20 batchwise. It is preferable to carry it out batchwise.

This process is advantageously applied to a brine. The term "brine" is understood to denote, conventionally, an aqueous sodium chloride (NaCl) solution in which one or more other constituents can  
25 optionally be present in smaller amounts. The process gives good results when it is applied to brines with a sodium chloride content of at least 100 g/l. Their maximum sodium chloride content is that which corresponds to saturation; in practice, their NaCl  
30 content generally does not exceed 300 g/l.

The organic compounds which the process according to the invention is targeted at removing are in particular the compounds of the following types: carboxylic acid (formic acid, acetic acid, and the  
35 like), alcohols (methanol, pentanol, and the like), aldehydes (acetaldehyde, and the like), amines (alanine, and the like) and in particular sulphur derivatives (dimethyl sulphide, dimethyl sulphoxide, trimethylsulphonium chloride, and the like). The

process gives particularly outstanding results when the solution to be purified comprises at least one sulphonium salt. The term "sulphonium salt" is understood to denote any compound of formula  
5  $(R_1R_2R_3S)_nX$ , where  $R_1$ ,  $R_2$  and  $R_3$  are identical or different and denote substituted or unsubstituted alkyl, aryl, aralkyl or alkaryl radicals and X denotes an anion with a valency of n. The X anion is generally a halogen, usually chlorine ( $n = 1$ ). The invention  
10 applies particularly to the case where the sulphonium salt is trimethylsulphonium chloride. In this case, good results were obtained with trimethylsulphonium chloride contents of the order of 50 to 280 mg/l, without these values, however, having a limiting  
15 nature.

In the process according to the invention, the solution to be purified can naturally exhibit a pH value equal to or greater than 13. This, however, is not generally the case and it is then necessary to  
20 bring the pH to at least 13 by addition of a strong base or by any equivalent means (for example, by electrochemical means). Use is preferably made of a water-soluble base, for example chosen from alkali metal hydroxides and salts (sodium carbonate, and the  
25 like). Alkali metal hydroxides are preferred, in particular sodium hydroxide (NaOH). The amount of strong base to be employed will depend on the solution to be purified, on its initial pH and on the desired pH. Advantageously, the content of strong base in the  
30 solution on conclusion of stage (a) is at least 10 mmol per kg of solution, preferably at least 300 mmol/kg.

During the heating stage (b), the temperature of the aqueous solution is advantageously brought to at least 120°C, without, however, exceeding its boiling  
35 temperature. Very good results were obtained above 130°C, for example at approximately 140°C. The duration of stage (b) is preferably from 2 to 6 hours. This stage advantageously takes place under autogenous

pressure, in order in particular to prevent the aqueous solution from boiling.

If the aqueous solution comprises a sulphonium salt, stages (a) and (b) have the effect of decomposing this salt to an alcohol, on the one hand, and to a sulphide, on the other hand. For example, in the case where the solution comprises trimethylsulphonium chloride, stage (b) generally results in the formation of methanol and dimethyl sulphide  $((CH_3)_2S)$ .

10 According to an advantageous alternative form, after stage (b), hydrochloric acid (HCl) is added to the solution. This makes it possible to reduce the amount of chlorine-comprising oxidizing agent used during stage (c). In this alternative form, the amount  
15 of hydrochloric acid employed is advantageously such that the pH of the solution is less than 5 or else greater than 9.

The oxidation stage (c) makes it possible to decompose most of the organic compounds still present  
20 in the aqueous solution (for example, methanol or dimethyl sulphide, or alternatively an organic acid, such as, for example, formic acid).

The chlorine-comprising oxidizing agent is added to the aqueous solution gradually, so as to  
25 prevent the formation of chlorates. To this end, the flow rate of chlorine-comprising oxidizing agent is preferably adjusted so that the total amount of oxidizing agent is introduced over 5 to 30 minutes.

The chlorine-comprising oxidizing agent used in  
30 stage (c) is advantageously chosen from chlorine gas ( $Cl_2$ ) and sodium hypochlorite ( $NaClO$ ). If a gaseous chlorine-comprising oxidizing agent is used, it can be employed in any conventional way, for example by sparging into the aqueous solution, if appropriate  
35 after dilution by means of an inert gas, such as nitrogen.

At the end of stage (c), the solution can equally well be acidic or basic. However, preferably, during stage (c), a sufficient amount of chlorine-

comprising oxidizing agent is added to the solution for the pH to become less than 2 and preferably less than 1. The production of a very low pH at the end of the reaction is advantageous in the sense that it results in a very thorough purification, even in the cases where the subsequent use of the purified aqueous solution requires a higher pH, for example in the region of 7 (neutral solution); to this end, use may be made of a conventional technique, for example reaction with a base.

According to an advantageous alternative form, in stage (a), the pH of the solution is brought to at least 13 by addition of an alkaline sodium derivative and the ratio of the number of chlorine atoms in the chlorine-comprising oxidizing agent which are added during stage (c) to the number of sodium atoms which are added during stage (a) is from 0.5 to 1.5.

Stages (a) and (b), on the one hand, and (c), on the other hand, take place in the same reactor or in separate reactors. The reactor or reactors used must be composed of or internally coated with a material exhibiting sufficient mechanical strength and chemical resistance, for example titanium.

Stage (c) can optionally be followed by one or more conventional purification stages, such as a filtration, an additional purification by means of active charcoal or by ozonization, and the like.

**Example**

One kg of brine comprising 270 g/l of sodium chloride, 60 mg/l of trimethylsulphonium chloride (TMSC) (that is to say, 19 mg C/l) and 383 mg/l of formic acid (HCOOH) (i.e., approximately 100 mg C/l), exhibiting an overall TOC of 232 mg C/l, had added to it 300 mmol (12 g) of NaOH and then the brine was heated at 130°C in a stirred autoclave under autogenous pressure (approximately 2.7 bar after 3 hours). After reacting for 3 hours, the TMSC concentration was reduced to 37% of its initial value. Chlorine was subsequently added in a large excess with respect to

the amount of organic compounds (total amount of chlorine: 7.06 g). After 15 minutes, the TOC was reduced to approximately 30 ppm (30 mg of organic carbon per litre), the TMS concentration being for its part reduced to a value below the threshold for quantification by capillary electrophoresis (< 5 mg/l). The formic acid was virtually completely consumed.

It was found that a gradual addition of chlorine (over approximately 25 minutes) made it possible to obtain a lower final chlorate content than in the case of a rapid addition. The final pH was 13.4 (pH normalized to room temperature).

CLAIMS

1. Process for the purification from organic compounds of an aqueous solution, according to which:
  - 5 (a) the pH of the solution is brought to at least 13;
  - (b) the solution is heated at at least 100°C for at least 1 hour;
  - (c) at least one chlorine-comprising oxidizing agent is gradually added to the solution.
- 10 2. Process according to Claim 1, in which the aqueous solution is a brine.
3. Process according to either of the preceding claims, in which the solution to be purified comprises at least one sulphonium salt.
- 15 4. Process according to one of the preceding claims, in which the pH of the solution is brought to at least 13 by addition of a strong base and the content of strong base in the solution on conclusion of stage (a) is at least 10 mmol per kg of solution.
- 20 5. Process according to one of the preceding claims, in which the pH of the solution is brought to at least 13 by addition of sodium hydroxide.
6. Process according to one of the preceding claims, in which the duration of stage (b) is from 2 to
- 25 6 hours.
7. Process according to one of the preceding claims, in which, after stage (b), hydrochloric acid (HCl) is added to the solution.
8. Process according to one of the preceding
- 30 claims, in which the chlorine-comprising oxidizing agent used in stage (c) is chosen from chlorine gas (Cl<sub>2</sub>) and sodium hypochlorite (NaClO).
9. Process according to one of the preceding claims, in which, during stage (c), a sufficient amount
- 35 of chlorine-comprising oxidizing agent is added to the solution for the pH to become less than 2.
10. Process according to one of the preceding claims, in which, in stage (a), the pH of the solution is brought to at least 13 by addition of an alkaline



sodium derivative and the ratio of the number of chlorine atoms in the chlorine-comprising oxidizing agent which are added during stage (c) to the number of sodium atoms which are added during stage (a) is from 0.5 to 1.5.

11. A process for the purification from organic compounds of an aqueous solution as  
5 hereinbefore described with reference to the Example.



Application No: GB 9908550.8  
Claims searched: 1 to 11

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## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): C1C (CJB, CRAX, CRCH, CRCX)

Int CI (Ed.6): C02F 1/02, 1/66, 1/76, 9/00

Other: On-line : WPI, EPODOC, JAPIO

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X Y	GB 1567767 BAYER. Whole document.	1, 5 to 7. Y - 10.
X Y	GB 1459284 BP CHEMICALS. Whole document.	1, 2, 6, 8. Y - 10.
Y	US 5445741 DILLA et al. Column 2, line 46 to column 4, line 27.	10.
X	WPI Abstract Accession No. 94-221535 & JP 6157007. GODO SHIGEN SANGYO KK.	1, 4, 6, 8.
Y	See accompanying abstract.	Y - 10.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.